

Electronic structure of Lanthanide oxides by hybrid density functionals

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The band structures of CeO_2 and the lanthanide sesquioxides (Ln_2O_3 , with $\text{Ln}=\text{La},\dots,\text{Lu}$) have been calculated by the three hybrid functionals HSE03, HSE06 and sX-LDA. These describe the strongly correlated f-electrons of the oxides as well as or better than the recently reported $\text{G}_0\text{W}_0\text{@LDA}+\text{U}$ results, and yield the correct band gaps and trends. The main band gap between the oxygen 2p states and lanthanide 5d states is nearly independent of the lanthanide and the minimum gap is controlled by the energies of the 4f states with respect to these band edges. The experimentally observed periodicity of band gaps for Ln_2O_3 arises from a decline of the f level energies across the lanthanide series. The sX-LDA method is found to be slightly better than HSE at predicting the 4f energies and thus the band gaps.

Lanthanide oxides are a group of compounds whose unique electronic properties allow important applications as a catalyst, catalyst support, high dielectric constant gate oxide, and other applications including dopants for lasers, materials for magneto-optic memory and colorants for special glasses. Many properties of lanthanide (Ln) oxides are determined by their semi-core 4f levels. While being mainly localized on the Ln atoms and not participating in bonding and electronic conduction, 4f shell electrons are available for optical absorption processes and can establish strong magnetic order. Intriguingly, many physical properties of the lanthanide sesquioxides X_2O_3 are found to be periodic in the series $\text{X}=\text{La},\dots,\text{Lu}$. Prokofiev *et al.*¹ have found from photoemission experiments that the band gaps show four distinct dips for Ce, Eu, Tb and Yb, which arise from the 4f levels entering the forbidden gap. On the other hand, the reduction of CeO_2 to Ce_2O_3 by release of an oxygen atom leads to the transfer of electrons to the 4f orbitals of the two Ce atoms, with the two single occupied 4f levels being pushed down deep into the electronic band gap. The proper description of the 4f electrons is thus of greatest importance for the correct prediction of the electronic and magnetic properties of these oxides.

It is well known²⁻⁴ that the common density functional theory (DFT) approaches of the local-density (LDA) and generalized gradient approximation (GGA) cannot properly describe the 4f electrons in rare-earth compounds. This problem arises from the lack of self-interaction cancellation in DFT. This leads to an artificial delocalization of the electronic wave-functions⁵ and contributes to the underestimation of the excitation energies. Hence, purely local approaches fail to reproduce both the magnitude and the periodicity of the band gaps of lanthanide sesquioxides and predict that Ce_2O_3 is metallic (LDA) or a small-gap semiconductor (GGA). The problem can be partly solved by adding an empirical Hubbard U potential for the 4f orbitals within the LDA+U/GGA+U approach, as in Loschen *et al.*⁶ and Jiang *et al.*⁴. A more sophisticated treatment is the GW method⁷, where many-body effects are introduced by an (energy-dependent) self-energy term $\Sigma(\vec{r},\vec{r}',\epsilon) \approx iG(\vec{r},\vec{r}',\epsilon)W(\vec{r},\vec{r}',\epsilon)$, with

a one-particle Green's function G and a dynamically screened Coulomb interaction W. Inclusion of this self-energy considerably improves the description of excited state properties, but it is expensive if it is carried out in a fully self-consistent way. GW is often used as a one-shot correction to the Kohn-Sham energies, using the LDA/GGA wave-functions (GW approximation/ G_0W_0). Jiang *et al.*⁴ have shown that G_0W_0 corrections to LDA+U ground states give improved agreement to experiments. Hybrid exchange-correlation functionals are an alternative, moderate cost method for including many-body effects into a one-particle description. They are included by mixing in a (statically screened) fraction of Hartree-Fock exchange into the LDA/GGA exchange-correlation, effectively cancelling the self-interaction effects. This gives a great improvement in the predicted electronic and magnetic properties⁸⁻¹⁵. Crucially, they are generalized Kohn-Sham functionals¹³ that allow a self-consistent calculation of ground state properties such as total energy and atomic forces, in contrast to G_0W_0 . We here test the performance of two different hybrid functionals, HSE and sX-LDA, as implemented in the CASTEP computational package¹⁶. HSE, which exists in two different flavors, HSE03¹⁰ and HSE06¹¹, substitutes 25% of error-function screened PBE exchange by the same amount Hartree-Fock exchange. On the other hand, sX-LDA^{12,13} divides LDA into short-range and long-range and replaces the short-range exchange part by Hartree-Fock exchange screened by the Thomas-Fermi dielectric function. We shall see that the different incorporation of non-local exchange into standard local functionals leads to interesting variations in the predicted band structures of the 15 Ln_2O_3 oxides and of CeO_2 . We show that our tested hybrid functionals are a vast improvement over LDA and GGA for all investigated materials and yield results en par with the $\text{G}_0\text{W}_0\text{@LDA}+\text{U}$ values⁴. Details about the computational procedure can be found elsewhere¹⁷. In a first step, we calculated the band structures and density of states of CeO_2 , where Ce donates all its 6s and 5d valence electrons to the oxygen atoms, while the ground state of the 4f orbitals was established to be a mixed valence state of $4f^0$ and $4f^1$

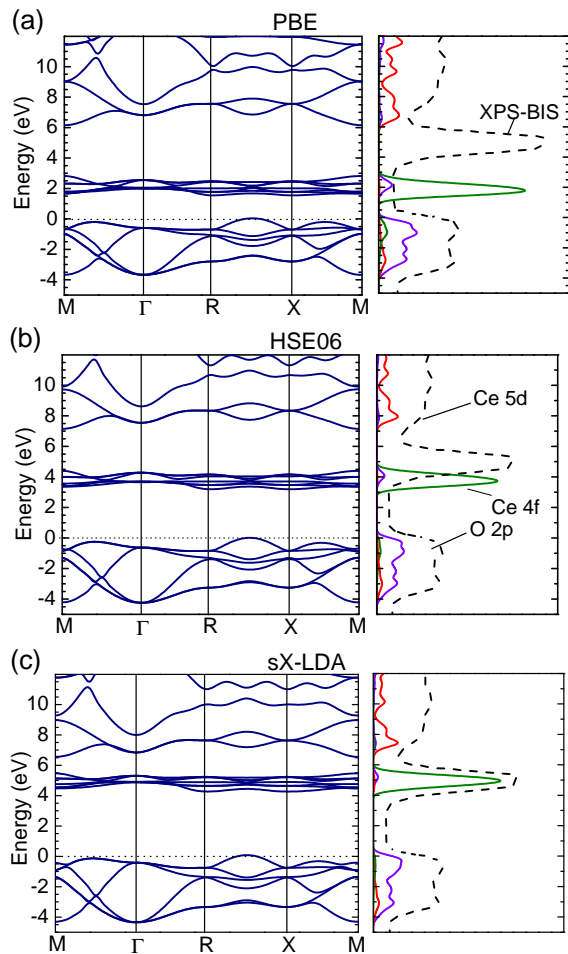


FIG. 1: (Color online) Band structures and (partial) density of states (DOS) of CeO_2 as calculated from the (a) PBE, (b) HSE06 and (c) sX-LDA exchange-correlation functionals. The dashed line in (a) depicts the experimentally measured DOS from Ref. [18] for comparison.

(\bar{v} is a ligand hole) configurations²³. This makes the valence band top O 2p in character, with a contribution from 4f states¹⁸. The lowest conduction band consists mainly of empty Ce 5d states starting at ≈ 6 eV above the valence band edge. Bremsstrahlung isochromat spectroscopy (BIS)¹⁸ and x-ray absorption spectroscopy²⁰ show a sharp peak below the conduction band, which was attributed to empty Ce 4f levels taking part in electron addition processes. Experimentally, the size of the band gap of CeO_2 is debated, in the range of 5.5-8 eV^{18,20-22}. Figure 1 compares the calculated band structures and partial density of states (DOS) of CeO_2 for the local exchange-correlation functional PBE and the three hybrid functionals HSE03, HSE06 and sX-LDA. The PBE valence band DOS agrees fairly well with experiment, although the predicted valence band width of 3.8 eV is slightly less than the experimental value of ≈ 4.4 eV. On the other hand, the failure of PBE becomes very clear for

TABLE I: Minimum band gaps (in eV) of CeO_2 as obtained from PBE, HSE, sX-LDA, B3LYP, PBE0 and $\text{G}_0\text{W}_0@LDA+U$ calculations and experiments.

Method/Property	p-f band gap	p-d band gap	VBM
PBE	1.5	6.2	3.8
HSE03	3.1, 3.5 ^{2,3}	6.9, 7 ^{2,3}	4.3
HSE06	3.4	7.2	4.3
sX-LDA	4.2	6.5	4.4
B3LYP ¹⁹	3.3	7.65	-
PBE0 ¹⁹	3.94	8.08	-
$\text{G}_0\text{W}_0@LDA+U^4$	4	6	4.4
Exp	3-3.5 eV ^{18,20}	5.5-8 ^{18,20-22}	≈ 4.5 -5 ^{18,20}

the unoccupied states. The 5d conduction band edge of 6.2 eV lies at the lower end of the experimental band gaps and, most strikingly, PBE vastly underestimates the energy of the 4f levels compared to the photoemission peak. Splitting the DOS into orbital contributions clearly shows the effect of the self-interaction, a considerable transfer of charge of the O^{2-} ions into the 4f orbitals due to mixing of O 2p and Ce 4f states at the valence band top, and the weakly dispersive gap states. This is reflected in the Mulliken populations of -0.63 e for the oxygen atoms and 1.27 e for the cerium atom.

Replacing the short-range part of the PBE exchange by Hartree-Fock exchange largely improves on the PBE results. For HSE06, the valence band is stretched by 0.5 eV to 4.3 eV, and is now in good agreement with the experimental DOS from x-ray photoelectron spectroscopy (XPS)¹⁸. The empty 4f states experience a strong shift by ≈ 2 eV, but still remain below the experimental peak. The higher energy of the 4f states renders mixing of 4f and O 2p states unfavourable, and corresponds to a slight delocalization of the empty 4f states and an accumulation of charge at the oxygen atoms, clearly shown in the partial DOS and the Mulliken population (O: 0.76 e, Ce: 1.53 e). The non-local exchange further produces a rigid shift of the conduction bands, opening the O 2p-Ce 5d band gap to 7.2 eV, well within the range of experimental band gaps. Compared to the studies of Hay *et al.*² and da Silva *et al.*³, our HSE03 calculations predict the Ce 5d states at slightly higher energies and the Ce 4f states at slightly lower energies, respectively. Indeed, it shows that the prediction of the 4f peak (and to a lesser extend for the 5d levels) is quite sensitive to the reference state of the Cerium pseudopotential. We thus specifically generated and used a tetravalent Cerium potential for our calculations on CeO_2 . We believe this causes the differences between our study and previous values.

sX-LDA pushes the 4f-levels to even higher energies than HSE06. This leads to a wide O 2p-Ce 4f gap of 4.1 eV, which is in perfect agreement with the experimental position of the dominant peak and with $\text{G}_0\text{W}_0@LDA+U$ data⁴. We further find a p-d band gap of 6.5 eV and a

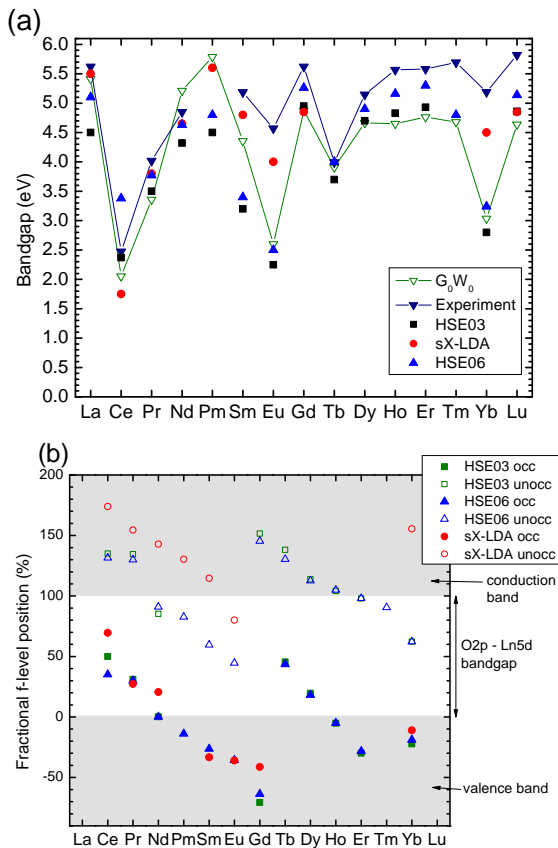


FIG. 2: (Color online) (a) Comparison of minimum electronic band gaps as obtained from calculations using the HSE03 (filled black squares), HSE06 (empty blue squares) and sX-LDA (filled red circles) calculations with experimental data (filled downward triangles) and the $G_0W_0@LDA+U$ results from Ref. [4] (empty upward triangles). (b) Positions of occupied (filled symbols) and unoccupied (empty symbols) f levels relative to VBM and CBM.

wider valence band of 4.4 eV. The weaker prediction of itinerant states, in this case the 5d levels, but more rigorous treatment of localized states compared to HSE06 has been observed for a variety of materials, *e.g.* transparent conducting oxides²⁴, and appears to be caused by the differences in short- and middle-range exchange between the two exchange-correlation functional types. Table I summarizes the obtained band gaps and valence band widths.

Similar predictions for the f-electrons are also found for lanthanide sesquioxides Ln_2O_3 with $Ln=La, \dots, Lu$. Prokofiev *et al.*¹ found that the optical band gaps show an unusual periodicity across the series with distinct dips for Ce, Eu, Tb and Yb oxides. While $LDA+U$ predicts the existence of dips in the band gaps, the detailed trends and sizes are not well reproduced. Jiang *et al.*⁴ showed that G_0W_0 corrections to $LDA+U$ ground states improve the predictions. Fig. 2 (a) shows the minimum band gaps

derived from our band calculations using the three hybrid functionals HSE03, HSE06 and sX-LDA compared to the G_0W_0 and experimental values. Clearly, the statically screened short-range Hartree-Fock exchange has a similar effect as G_0W_0 corrections and gives significant improvements on the local functionals, both for experimental trends and band gap sizes. We find that all three functionals fully restore the periodicity of the band gaps with the four observed dips and the 'plateau' between Ho₂O₃ and Tm₂O₃. The different performance of the hybrid functionals compared to $G_0W_0@LDA+U$ and experiments is closely related to the energy of the 4f electrons. Fig. 2 (b) shows the predicted energy of the highest filled and empty f-levels relative to the valence band maximum and conduction band minimum for the tested hybrid functionals. In accordance to the interpretation of Prokofiev *et al.*¹, the energies of the f-level energies decreases linearly across the series between the Ce-Gd oxides, from within the conduction band to deep into the valence band. The f-shells reach half-filling at Gd₂O₃ and the process then repeats. The minimum band gaps then correspond three different kinds of transitions, depending on the lanthanide. For the first materials in the series, the minimal gap arises from intra-atomic transitions between the occupied Ln 4f states and the Ln 5d states, which make up the bottom of the conduction band. At some point of the series, empty 4f levels enter the O2p-Ln5d band gap, while the filled 4f states are pushed into the valence band. The minimum band gap then changes to an inter-atomic transition from O 2p states to empty Ln 4f states. In addition, for Lanthanum, Lutetium and

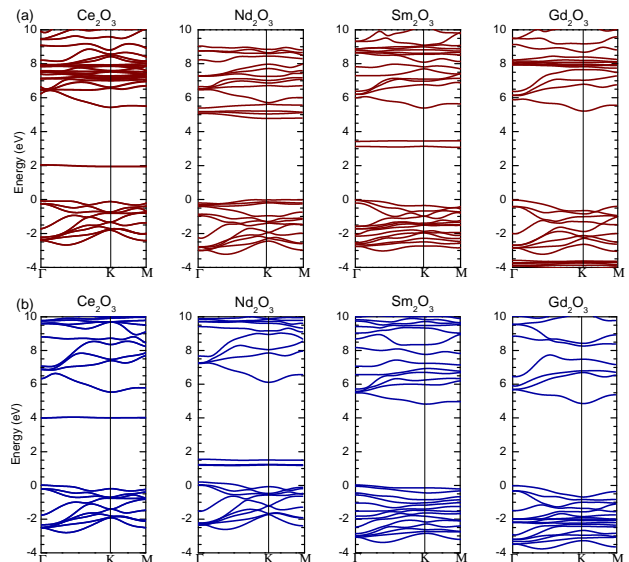


FIG. 3: (Color online) (a) and (b) band structures of selected lanthanide oxides from HSE06 and sX-LDA calculations, respectively. We chose the maximum of the oxygen 2p bands as the zero energy for a better comparison of the various band structures.

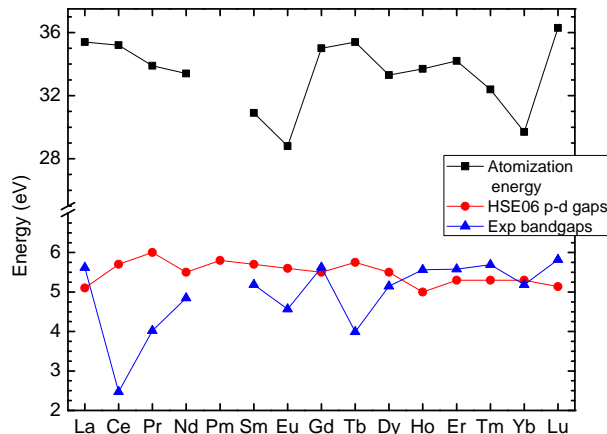


FIG. 4: (Color online) Comparison of the trends of the experimentally measured atomization energy (black squares) and band gaps (blue triangles) of 14 lanthanide sesquioxides, taken from Ref. [1] with the values of the band gaps between oxygen 2p and lanthanide 5d states as predicted from HSE06 calculations (red circles).

Gadolinium, there are no f-bands in the gap, the lowest transition is then O 2p-Ln 5d.

The HSE functionals systematically predict the f-bands to lie at lower energies in the forbidden gap than $G_0W_0@LDA+U$ and sX-LDA (see also band structures in Fig. 3). For the oxides with 4f-5d transitions, this automatically leads to the superior HSE06 band gaps, provided that the sizes of the forbidden gap from HSE06 and G_0W_0 are comparable. On the other hand, the lower energies of empty f-level lower the minimum band gaps

of oxides with predicted 2p-4f transitions, particularly Sm_2O_3 , Eu_2O_3 and Yb_2O_3 . This leads to considerable discrepancies with the experimentally measured values. Prokofiev *et al.*¹ attributed the minima for Eu_2O_3 and Yb_2O_3 to inter-atomic 2p-5d transitions due to the observed minima in the atomization energy for these materials. Their reasoning was that inter-atomic optical excitations, such as the O 2p-Ln 5d transition, cause a partial break of the Ln-O bonds and should thus correlate with the bond/atomization energies. In contrast, the HSE06 2p-5d band gaps are fairly independent of the lanthanide, see Fig. 4, and, above all, show no minima for Eu_2O_3 and Yb_2O_3 . Hence, the observed minima in HSE arise *purely* from the relative energy of empty f-states in the gap.

sX-LDA shows a qualitatively different behavior for some of the oxides. It is clear from Fig. 2 (b) that sX-LDA again predicts the empty f-levels at considerably higher energies than HSE (and $G_0W_0@LDA+U$); they always are within the bulk conduction band, except for Eu_2O_3 . Correspondingly, the minimum band gaps for Pm_2O_3 , Sm_2O_3 and Yb_2O_3 are of 2p-5d nature and in much better agreement with experiment compared to HSE and $G_0W_0@LDA+U$. This effect is somewhat counteracted by the energetically lower onset of the Ln 5d bands for most materials along the series, similar to the case of CeO_2 . While this keeps most of the band gaps on HSE level, sX-LDA seems to perform particularly well for compounds with empty f-levels in the bulk band gap.

In summary, the three hybrid functionals are found to be comparable or superior to $G_0W_0@LDA+U$ for the prediction of the band gaps of lanthanide oxides. For lanthanide sesquioxides, this is due to the incorrect ground states from $LDA+U$ calculations, which yield roughly the correct trends but heavily underestimate the band gap sizes. Electronic ground states from hybrid functionals might be better starting points for self-energy corrections.

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- ¹⁷ We modeled all 15 lanthanide sesquioxides by the hexagonal (A-type) structure of space group P-3m1 and imposed antiferromagnetic order on the f-electrons. CeO_2 was modeled by the three atom primitive cell of the cubic fluorite structure (space group Fm-3m). The atomic cores were described by norm-conserving pseudopotentials generated by the OPIUM code. We treated the (4f,5s,5p,5d,6s) states as valence states by plane waves with a cutoff energy of 750 eV. Reciprocal space integration was performed by k-point grids of 4x4x3 and 4x4x4 k-points in the Brillouin

zone of Ln_2O_3 and CeO_2 , respectively. We optimized the geometry at the GGA level preserving the symmetry of the system until the pressure on the unit cell was below 0.01 GPa and the residual forces between the atoms was below 0.01 eV/Å. The density of states were calculated by a grid of 10x10x10 equally spaced points in the Brillouin zone.

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